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# Theoretical fine spectroscopy with symmetry-adapted-cluster configuration-interaction method: Outer- and inner-valence ionization spectra of furan, pyrrole, and thiophene

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Theoretical fine spectroscopy has been performed for the valence ionization spectra of furan, pyrrole, and thiophene with the symmetry-adapted-cluster configuration-interaction general- $R$  method. The present method described that the  $\pi_1$  state interacts with the  $\pi_3^{-2}\pi^*$ ,  $\pi_2^{-2}\pi^*$ , and  $\pi_2^{-1}\pi_3^{-1}\pi^*$  shake-up states providing the split peaks and the outer-valence satellites, both of which are in agreement with the experiments. The intensity distributions were analyzed in detail for the inner-valence region. In particular, for furan, theoretical intensities were successfully compared with the intensity measured by the electron momentum spectroscopy. The interactions of the  $3b_2$  and  $5a_1$  states with the shake-up states were remarkable for furan and pyrrole, while the  $4b_2$  state of thiophene had relatively large intensity. © 2005 American Institute of Physics.  
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## I. INTRODUCTION

Chemistry involving the excited and ionized states shows a rich variety of phenomena that are both characteristic and interesting. These phenomena can be understood with the precise knowledge of the electronic structure of molecules, and therefore, accurate theoretical description of these states has been an important and challenging subject. The symmetry-adapted-cluster<sup>1</sup> (SAC) symmetry-adapted-cluster configuration-interaction<sup>2-7</sup> (SAC-CI) method has been well established as a useful quantum-chemical method<sup>8</sup> for studying molecular ground, excited, ionized, and electron-attached states and has been successfully applied to wide varieties of chemistry. As one of the extensive applications, we have been exploiting theoretical fine spectroscopy with the SAC-CI method.

The excitation and ionization spectra of five-membered ring molecules, furan, pyrrole, and thiophene, have been

widely studied both theoretically and experimentally, since these systems are fundamental units in various important biological systems. On the theoretical side, pioneering theoretical spectroscopy for the molecules was performed by the SAC-CI method<sup>9</sup> and was followed by many theoretical works.<sup>10-18</sup> In our previous works,<sup>17,18</sup> accurate excitation spectra of the molecules were calculated with the sufficiently flexible basis sets of valence and Rydberg functions; the detailed assignments were proposed for the ultraviolet (UV) and vacuum ultraviolet (VUV) regions up to ionization threshold. We are aiming at the consistent interpretations of the electronic spectra of these molecules and therefore, we expand application of theoretical fine spectroscopy into the valence ionization spectra.

Experimentally, several methods<sup>19-21</sup> have been employed for the study of the valence ionization spectra of the molecules at issue. Ionization spectra for the outer-valence region of the molecules were measured by He I and He II photoelectron spectroscopy (PES),<sup>19,22-27</sup> followed by synchrotron-radiation PES (SRPES) measurement<sup>28</sup> that covered the inner-valence region up to about 40 eV. Very re-

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cently, high-energy-resolution SRPES study<sup>29</sup> was reported, providing band assignments with the help of the Green's-function calculations. Penning ionization electron spectroscopy (PIES) is another means to measure high-energy-resolution ionization spectra and was applied to outer-valence region of furan and pyrrole for which experimental band assignments were made by taking advantage of collision-energy dependence of the cross section.<sup>30</sup> Binary (*e,2e*) spectroscopy or electron momentum spectroscopy (EMS) is also known as a powerful tool for the study of the valence ionization spectra. Although the energy resolution obtainable is not satisfactory compared with those of PES and PIES, the unique ability of EMS to experimentally determine symmetries and monopole intensities for individual transitions was applied to furan<sup>31</sup> and pyrrole.<sup>32</sup>

In spite of the abundance of the experimental studies, however, there is still the subject of controversy, in particular, concerning the band position of the outer-valence  $\pi_1$  orbital. There are two reasons behind this. Firstly, the  $\pi_1$  band has not been energetically resolved from the adjacent bands even in the high-energy-resolution ionization spectra. Secondly, although a number of theoretical calculations<sup>9–12,27–34</sup> were made, the theoretical band assignments have been diverse. Furthermore, for the inner-valence region there have been no theoretical calculations that show a fair agreement with the experimental ionization spectra. Clearly, accurate theoretical study by the more advanced method with sufficient basis set would be required for the clarification of the valence ionization spectra of the molecules.

Recently, we have systematically applied the SAC-CI general-*R* method<sup>35,36</sup> to the valence ionization spectra.<sup>37–43</sup> For ordinary single electron ionization processes, the SAC-CI singles and doubles (SD)-*R* method is reliable, but for multiple-electron processes involved in the shake-up satellites, the general-*R* method has been shown to be a powerful tool. In the present work, we investigate the valence ionization spectra of furan, pyrrole, and thiophene for the accurate assignments of the main and satellite peaks. We compare our results with the experimental spectra by SRPES,<sup>28,29</sup> EMS,<sup>31,32</sup> and PIES+He I PES.<sup>30</sup> The results of the critical analysis of the intensity distributions in the inner-valence region are directly compared with those by EMS.

## II. COMPUTATIONAL DETAILS

The basis sets were selected as flexible to describe the electron correlations of the valence ionized states; the valence triple zeta of Schafer *et al.*<sup>44</sup> was used, namely, [5s3p] Gaussian-type orbitals (GTOs) augmented with *d*-type polarization function of  $\zeta_d=0.75, 0.80$ , and  $0.85$  for C, N, and O, respectively, [5s4p] GTOs plus *d*-type polarization function of  $\zeta_d=0.421$  for S atom, and [3s] for H atom. The effect of Rydberg functions on the theoretical spectra was small with the preliminary calculations; the convoluted spectra were almost unchanged, therefore, they were not included. The resultant self-consistent-field (SCF) dimensions were 107, 110,

and 110 for furan, pyrrole, and thiophene, respectively. Geometries of these molecules were due to the experimental ones.<sup>45</sup>

The SAC-CI general-*R* calculations were performed for the vertical ionization spectra. The 1s orbitals of C, N, and O and 1s, 2s, and 2p orbitals of S were taken as the core molecular orbitals (MOs) and were excluded from the active space. The resultant SAC-CI active spaces were 13 occupied and 89 unoccupied MOs for furan, 13 occupied and 92 unoccupied MOs for pyrrole, 13 occupied and 88 unoccupied MOs for thiophene. Most of the shake-up states were found to be dominantly described by two-electron processes, and therefore the *R* operators were included up to triples. In order to reduce the computational effort, perturbation selection was carried out in the perturbative way.<sup>7</sup> The LevelOne accuracy in GAUSSIAN03 (Ref. 8) was adopted as follows. Since large numbers of ionized states were calculated, sufficient operators were selected with this level of accuracy. The threshold of the linked terms for the ground state was set to  $\lambda_g=1 \times 10^{-5}$ . The unlinked terms were described as the products of the important linked terms whose SDCI coefficients were larger than 0.005. For ionized state, the thresholds of the linked doubles and triples were set to  $\lambda_e=1 \times 10^{-6}$  and  $\lambda_e=5 \times 10^{-6}$ , respectively. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.1 and 0.0 for the *R* and *S* operators, respectively.

The ionization cross sections were calculated using the monopole approximation<sup>46,47</sup> to estimate the relative intensities of the peaks. For the calculations of monopole intensities, the correlated SAC/SAC-CI wave functions were used for the ground and ionized states to include both the initial-state correlation and final-ionic-state correlation. The general-*R* spectra were convoluted with Gaussian envelope for describing the Franck–Condon widths and the resolution of spectrometer; the full width at half maximum (FWHM) of Gaussian was adopted as 0.08 (in eV).

The SAC/SAC-CI calculations were executed using the SAC-CI program system, which has been incorporated into the recently distributed GAUSSIAN03 suite of programs.<sup>8</sup>

## III. IONIZATION SPECTRUM OF FURAN

First, we discuss the valence ionization spectrum of furan. The valence electronic orbital sequence of furan is given by

$$\begin{aligned} &(\text{core})(4a_1)(5a_1)(3b_2)(4b_2)(6a_1)(7a_1)(1b_1)(5b_2)(6b_2) \\ &\times (8a_1)(9a_1)(2b_1)(1a_2), \end{aligned}$$

where the ionizations from the  $4a_1$ ,  $5a_1$ , and  $3b_2$  orbitals appear in the inner-valence region. The general-*R* calculations were performed to simulate the spectrum up to about 36 eV; for this purpose, 170, 5, 20, and 80 solutions were solved for  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  symmetries, respectively, since the peak intensities of  $A_1$  and  $B_2$  symmetries were distributed up to high-energy region. In Fig. 1, the calculated spectrum was compared with the SRPES (Ref. 29) and EMS (Ref. 31) spectra in both the outer- and inner-valence regions. Table I summarizes the ionization potentials (IPs), monopole inten-

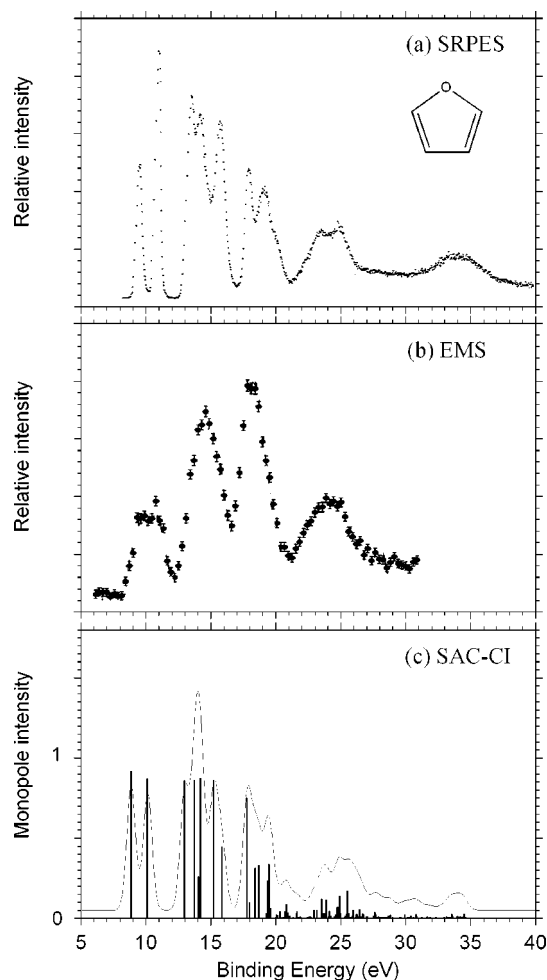


FIG. 1. Valence ionization spectra of furan by (a) SRPES (Ref. 29), (b) EMS (Ref. 31), and (c) SAC-CI general-*R* method.

sities, and the dominant configurations calculated by the general-*R* method. Experimental IPs by He I PES,<sup>19,30</sup> SRPES,<sup>28</sup> and EMS (Ref. 31) were also given with the EMS intensities.<sup>31</sup> Note that we gave the values only for the ionized states whose intensity is larger than 0.025 and that there are many other states with small intensity.

As noted in the Introduction, different assignments originating in the position of the  $1b_1(\pi_1)$  state were proposed for the outer-valence region. First two peaks were unanimously assigned to the  $1a_2(\pi_3)$  and  $2b_1(\pi_2)$  states. For the next peak, a cluster of adjacent electronic states exists and the following three types of the assignments were proposed:

- (I)  $9a_1 < 8a_1 < 6b_2 < 5b_2 < 1b_1(\pi_1)$ ,
- (II)  $9a_1 < 8a_1 < 6b_2 < 1b_1(\pi_1) < 5b_2$ ,
- (III)  $9a_1 < 1b_1(\pi_1) < 8a_1 < 6b_2 < 5b_2 < 1b_1(\pi_1)$ .

The ordering I was obtained by the outer-valence Green's-function (OVGF) calculation<sup>33</sup> and the PIES study.<sup>30</sup> The previous SAC-CI study<sup>9</sup> and the multireference single and double (MRD)-CI calculation<sup>10</sup> gave the ordering II, while the EMS experiment<sup>31</sup> suggested the ordering III, in which the  $1b_1(\pi_1)$  state splits into two peaks. Recent algebraic diagrammatic construction ADC(3) calculation also gave split peaks, though the intensity of the lower state was very

small.<sup>29</sup> This situation shows that the accurate calculation is necessary for the reliable assignments in this energy region. In the present calculation, the  $1b_1(\pi_1)$  state dominantly splits into two peaks by the interaction with the two-electron process,  $1a_2(\pi_3)^{-2}3b_1(\pi^*)$ ; they were calculated at 14.03 and 15.84 eV with the intensities of 0.26 and 0.45, respectively. This agrees with the EMS experiment<sup>31</sup> where two peaks were suggested at 13.6 and 15.6 eV with the equal intensity. Thus, the ordering in this region was calculated to be

$$9a_1 < 8a_1, 1b_1(\pi_1) < 6b_2 < 5b_2 < 1b_1(\pi_1).$$

Other  $B_1$  shake-up states were also obtained with small intensities in the region of 18–20 eV; these states were characterized as  $2b_1(\pi_2)^{-2}3b_1(\pi^*)$  and  $2b_1(\pi_2)^{-1}2a_2(\pi^*)1a_2(\pi_3)^{-1}$  states.

In the higher-energy region of 17.5–22.5 eV, two peaks were observed by the SRPES study,<sup>29</sup> which correspond to the ionizations from the  $7a_1$ ,  $6a_1$ , and  $4b_2$  orbitals. In Fig. 2, for analyzing the spectrum, the intensity contributions from the  $7a_1$ ,  $6a_1$ ,  $5a_1$ ,  $4b_2$ , and  $3b_2$  orbitals were shown for the energy region of 16–32 eV. The  $7a_1$  state was calculated to be single peak at 17.77 eV, while the  $6a_1$  and  $4b_2$  states split into two peaks with small energy separation due to the interaction with the  $1a_2^{-2}12a_1$  and  $2b_1^{-1}12a_11a_2^{-1}$  states, respectively. These states were calculated at 18.40 and 18.69 eV and 19.37 and 19.46 eV, which agree well with the experimental values of 18.8 and 19.7 eV,<sup>31</sup> respectively.

Some shake-up states were also obtained in the higher-energy region of the  $4b_2$  peak; their intensities originate mostly in the  $4b_2$  orbital. These states are dominantly described by  $6b_2^{-1}2a_21a_2^{-1}$  and  $2b_1^{-1}10a_11a_2^{-1}$ . In the EMS work, the observed (*e*, 2*e*) cross sections were analyzed in terms of monopole intensity not only for the main peaks but also for the satellite peaks. According to the EMS analysis, the intensity of the satellite at 21.9 eV was attributed to the  $4b_2$ ,  $7a_1$ , and  $3b_2$  orbitals, whose contributions were evaluated as 0.25, 0.10, and 0.10, respectively.<sup>31</sup> In the present calculations, dominant contributions were due to the  $4b_2$  orbital with the total intensity of 0.17 and other small contributions were from the  $7a_1$  shake-up state at 20.91 eV with the intensity of 0.04 and from the  $3b_2$  state at 21.57 eV with the intensity of 0.03.

In the inner-valence region, the breakdown of the orbital picture is prominent and the intensities due to the  $3b_2$  and  $5a_1$  orbitals distribute among many shake-up states, as shown in Figs. 1 and 2. The satellite peak observed at 23.1 eV with the intensity of 0.25( $3b_2$ )+0.10( $6a_1$ ) (Ref. 31) was mainly attributed to the shake-up states of  $b_2$  symmetry calculated at 22.93, 23.52, and 23.89 eV with the total intensity of 0.28. In the energy region of the peak at 24.6 eV, the shake-up states of different symmetry were calculated at 24.76 and 24.91( $3b_2$ ) and 24.75, 24.99, and 25.53 eV( $5a_1$ ), whose total intensities were 0.18 and 0.27, respectively; this agrees with the EMS assignment and the estimated EMS intensities were 0.10( $3b_2$ ) and 0.25( $5a_1$ ). The satellites observed at 26.2 eV were characterized as the  $5a_1$  and  $3b_2$  by EMS and their intensities were evaluated as 0.20 and 0.25, respectively.<sup>31</sup> In the present calculation, dominant contribution was due to the  $5a_1$  calculated at 25.95–27.61 eV with

TABLE I. Ionization potentials (IPs) (in eV), monopole intensities (in parenthesis), and main configurations of the outer- and inner-valence ionized states of furan. Ionized states whose intensity is larger than 0.025 are shown.

State	Expt.				SAC-CI general-R	
	He I PES <sup>a</sup>	He I PES <sup>b</sup>	SRPES <sup>c</sup>	EMS <sup>d</sup>	IP (Intensity)	Main configuration ( $ C  \geq 0.4$ ) <sup>e</sup>
1a <sub>2</sub>	8.78	9.11	9.0	9.0 (0.95)	8.83 (0.92)	0.93(1a <sub>2</sub> <sup>-1</sup> )
2b <sub>1</sub>	10.38	10.48	10.4	10.4 (0.90)	10.10 (0.87)	0.91(2b <sub>1</sub> <sup>-1</sup> )
9a <sub>1</sub>	12.94	13.10	13.0	13.0 (~1)	12.94 (0.86)	0.87(9a <sub>1</sub> <sup>-1</sup> )
8a <sub>1</sub>	13.84	13.74	13.6	13.8 (~1)	13.73 (0.86)	0.87(8a <sub>1</sub> <sup>-1</sup> )
6b <sub>2</sub>	14.47	14.46	14.2	14.4 (~1)	14.21 (0.87)	0.90(6b <sub>2</sub> <sup>-1</sup> )
5b <sub>2</sub>	15.20	15.18	15.2	15.2 (~1)	15.21 (0.86)	0.90(5b <sub>2</sub> <sup>-1</sup> )
1b <sub>1</sub>	(15.2)	15.44	15.6	13.6 (0.50)	14.03 (0.26)	0.50(1b <sub>1</sub> <sup>-1</sup> ) + 0.72(1a <sub>2</sub> <sup>-2</sup> 3b <sub>1</sub> )
				15.6 (0.50)	15.84 (0.45)	0.66(1b <sub>1</sub> <sup>-1</sup> ) - 0.49(1a <sub>2</sub> <sup>-2</sup> 3b <sub>1</sub> )
					17.97 (0.10)	0.70(2b <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> ) + 0.48(2b <sub>1</sub> <sup>-2</sup> 3b <sub>1</sub> )
					19.28 (0.03)	0.90(1a <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 2b <sub>1</sub> <sup>-1</sup> ) + 0.51(2b <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> )
					20.32 (0.05)	0.66(2b <sub>1</sub> <sup>-2</sup> 3b <sub>1</sub> ) - 0.44(2b <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> )
7a <sub>1</sub>	17.77	17.49	17.5	17.5	17.77 (0.75)	0.84(7a <sub>1</sub> <sup>-1</sup> )
				(0.75 + 0.25)		
				21.9 (0.10)	20.91 (0.04)	0.47(2b <sub>1</sub> <sup>-1</sup> 3b <sub>1</sub> 9a <sub>1</sub> <sup>-1</sup> ) - 0.44(1a <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 9a <sub>1</sub> <sup>-1</sup> ) + 0.41(1a <sub>2</sub> <sup>-1</sup> 3b <sub>1</sub> 6b <sub>2</sub> <sup>-1</sup> )
					23.15 (0.03)	0.77(1a <sub>2</sub> <sup>-1</sup> 3b <sub>1</sub> 5b <sub>2</sub> <sup>-1</sup> )
					24.13 (0.05)	0.41(2b <sub>1</sub> <sup>-1</sup> 3b <sub>1</sub> 8a <sub>1</sub> <sup>-1</sup> )
6a <sub>1</sub>		18.68	18.7	18.8	18.40 (0.31)	0.54(6a <sub>1</sub> <sup>-1</sup> )
				(0.75 + 0.10)	18.69 (0.33)	0.55(6a <sub>1</sub> <sup>-1</sup> ) + 0.51(1a <sub>2</sub> <sup>-2</sup> 12a <sub>1</sub> )
				19.7 (0.05)	19.60 (0.06)	0.65(1a <sub>2</sub> <sup>-2</sup> 10a <sub>1</sub> )
				23.1 (0.10)	23.15 (0.03)	0.77(1a <sub>2</sub> <sup>-1</sup> 3b <sub>1</sub> 5b <sub>2</sub> <sup>-1</sup> )
					23.70 (0.03)	0.47(1a <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 9a <sub>1</sub> <sup>-1</sup> )
4b <sub>2</sub>			19.8	19.7 (0.65)	23.78 (0.03)	0.48(2b <sub>1</sub> <sup>-2</sup> 13a <sub>1</sub> )
					19.37 (0.24)	0.47(4b <sub>2</sub> <sup>-1</sup> ) + 0.37(2b <sub>1</sub> <sup>-1</sup> 12a <sub>1</sub> 1a <sub>2</sub> <sup>-1</sup> )
					19.46 (0.34)	0.57(4b <sub>2</sub> <sup>-1</sup> ) - 0.32(2b <sub>1</sub> <sup>-1</sup> 12a <sub>1</sub> 1a <sub>2</sub> <sup>-1</sup> )
					20.72 (0.04)	0.59(6b <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> ) + 0.44(6b <sub>2</sub> <sup>-1</sup> 3b <sub>1</sub> 2b <sub>1</sub> <sup>-1</sup> )
					20.79 (0.09)	0.48(6b <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> )
3b <sub>2</sub>			21.9	21.9 (0.25)	21.63 (0.04)	0.55(1a <sub>2</sub> <sup>-1</sup> 10a <sub>1</sub> 2b <sub>1</sub> <sup>-1</sup> ) + 0.47(2b <sub>1</sub> <sup>-1</sup> 10a <sub>1</sub> 1a <sub>2</sub> <sup>-1</sup> )
				21.9 (0.10)	21.57 (0.03)	0.50(1a <sub>2</sub> <sup>-1</sup> 3b <sub>1</sub> 8a <sub>1</sub> <sup>-1</sup> )
					22.93 (0.05)	0.46(2b <sub>1</sub> <sup>-1</sup> 3b <sub>1</sub> 5b <sub>2</sub> <sup>-1</sup> )
				23.1	23.52 (0.12)	0.35(3b <sub>2</sub> <sup>-1</sup> ) + 0.37(1a <sub>2</sub> <sup>-2</sup> 10b <sub>2</sub> )
					23.89 (0.11)	0.34(3b <sub>2</sub> <sup>-1</sup> ) + 0.38(8a <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 2b <sub>1</sub> <sup>-1</sup> )
					24.76 (0.04)	0.54(2b <sub>1</sub> <sup>-1</sup> 3b <sub>1</sub> 6b <sub>2</sub> <sup>-1</sup> ) + 0.45(1a <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 6b <sub>2</sub> <sup>-1</sup> )
					24.91 (0.14)	0.37(3b <sub>2</sub> <sup>-1</sup> ) + 0.41(2b <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 9a <sub>1</sub> <sup>-1</sup> )
					24.45 (0.03)	0.50(2b <sub>1</sub> <sup>-2</sup> 7b <sub>2</sub> )
				26.2	25.63 (0.03)	0.50(2b <sub>1</sub> <sup>-2</sup> 8b <sub>2</sub> )
					25.93 (0.04)	0.66(1a <sub>2</sub> <sup>-1</sup> 2a <sub>2</sub> 5b <sub>2</sub> <sup>-1</sup> )
5a <sub>1</sub>			24.6	24.6 (0.25)	24.75 (0.07)	0.52(2b <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 6b <sub>2</sub> <sup>-1</sup> )
					24.99 (0.03)	0.58(4b <sub>2</sub> <sup>-1</sup> 3b <sub>1</sub> 1a <sub>2</sub> <sup>-1</sup> )
					25.53 (0.17)	0.40(5a <sub>1</sub> <sup>-1</sup> ) - 0.41(2b <sub>1</sub> <sup>-1</sup> 3b <sub>1</sub> 6a <sub>1</sub> <sup>-1</sup> ) + 0.41(6a <sub>1</sub> <sup>-1</sup> 3b <sub>1</sub> 2b <sub>1</sub> <sup>-1</sup> )
					25.95 (0.05)	0.55(2b <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 5b <sub>2</sub> <sup>-1</sup> )
				26.2	26.23 (0.03)	0.44(1b <sub>1</sub> <sup>-1</sup> 7b <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> )
4a <sub>1</sub>					26.46 (0.05)	0.35(7a <sub>1</sub> <sup>-1</sup> 2a <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> )
					26.69 (0.03)	0.61(2b <sub>1</sub> <sup>-2</sup> 14a <sub>1</sub> )
					27.61 (0.04)	0.38(2b <sub>1</sub> <sup>-1</sup> 12b <sub>2</sub> 1a <sub>2</sub> <sup>-1</sup> )
				29.7	30.80 (0.03)	0.68(2b <sub>1</sub> <sup>-1</sup> 4b <sub>1</sub> 8a <sub>1</sub> <sup>-1</sup> )
				33.5	33.52 (0.03)	—
					34.52 (0.03)	—

<sup>a</sup>Reference 19.<sup>b</sup>Reference 30.<sup>c</sup>Reference 28.<sup>d</sup>Reference 31.<sup>e</sup>Main configurations with the coefficients of  $|C| \geq 0.4$  are shown; “—” means there are no main configurations.



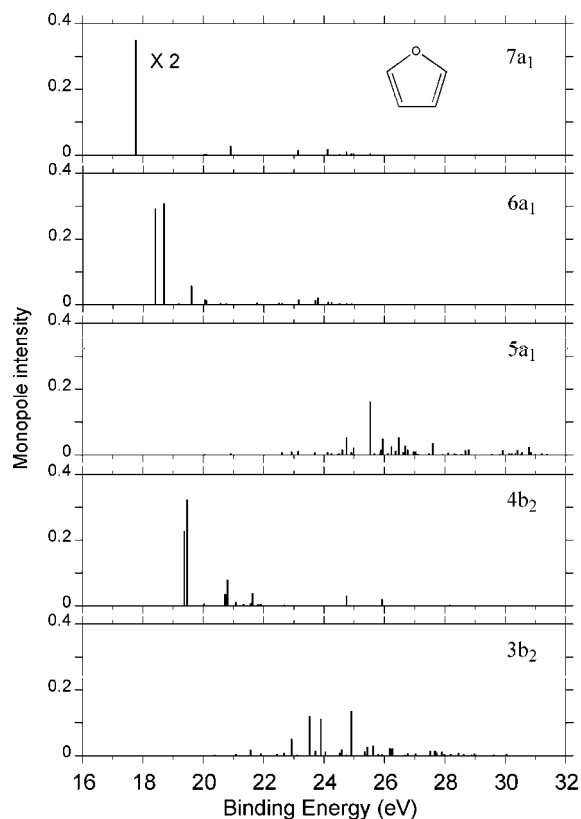


FIG. 2. MO contributions to monopole intensities in the energy region of 16–32 eV for furan.

the total intensity of 0.20 and the shake-up states of the  $3b_2$  component were also obtained at 25.45, 25.63, and 25.93 eV with the total intensity of 0.1. In the energy region of the peak observed at 29.7 eV, many satellites with small intensities, most of which were not given in Table I, were calculated. Many shake-up states whose intensities originate in the  $4a_1$  orbital were also obtained in the energy region around 33.5 eV; this peak is located higher in energy than those of pyrrole and thiophene.

In Fig. 3, the intensity contributions from the  $a_1$  or  $b_2$  component are compared between the SAC-CI and EMS. In the low-energy region of the satellite spectrum, the  $a_1$  component is dominant, while the  $b_2$  contribution is large in the high-energy region. Note that the EMS intensities involve contributions from the shake-off processes that produce the doubly ionized molecular ion. Nevertheless, one can see from the figure that the SAC-CI and EMS results are consistent with each other in the details of the satellite structure.

#### IV. IONIZATION SPECTRUM OF PYRROLE

Next, outer- and inner-valence ionization spectra of pyrrole are discussed. The SAC-CI spectrum was calculated up to about 32 eV. Figure 4 compares the theoretical spectrum with the SRPES (Ref. 29) and EMS (Ref. 32) spectra. More detailed intensity contributions in the energy region of 16–32 eV were shown in Fig. 5. Table II summarizes the results of the SAC-CI general- $R$  method in comparison with

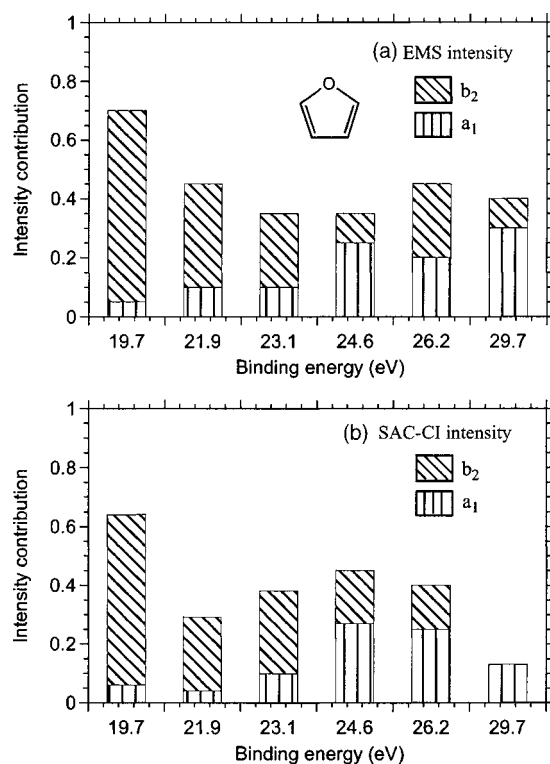


FIG. 3. Intensity contributions from the  $a_1$  and  $b_2$  orbitals for the satellites of furan; comparison between the (a) EMS (Ref. 31) and (b) SAC-CI.

the experimental IPs by He I PES+PIES,<sup>30</sup> He II PES,<sup>23</sup> and EMS;<sup>32</sup> the experimental values were reported only in the outer-valence region.

Different assignments have also been proposed for the outer-valence region of pyrrole. First two peaks observed at 8.28 and 9.26 eV by He I PES (Ref. 30) were assigned to the  $1a_2$  and  $2b_1$  states. For the next two peaks in the region of 12.5–15.0 eV, four different assignments exist with respect to the  $1b_1(\pi_1)$  states; the controversy is reminiscent of that for furan. The OVGf (Ref. 34) and the previous SAC-CI SD- $R$  calculations<sup>9</sup> gave the assignment of

$$(I) 9a_1 < 6b_2 < 1b_1 < 5b_2 < 8a_1,$$

while the MRD-CI calculation<sup>11</sup> predicted different sequence as

$$(II) 1b_1 < 9a_1 < 6b_2 < 5b_2 < 8a_1.$$

The He I PES+PIES study<sup>30</sup> suggested different ordering,

$$(III) 9a_1 < 1b_1 < 6b_2 < 5b_2 < 8a_1,$$

and the sequence,

$$(IV) 1b_1 < 9a_1 < 6b_2 < 1b_1 < 5b_2 < 8a_1,$$

was proposed by the EMS experiment.<sup>32</sup>

The present general- $R$  method calculated the main lines at 12.61( $9a_1$ ), 12.77( $1b_1$ ), 13.35( $6b_2$ ), 14.49( $5b_2$ ), and 14.57( $8a_1$ ) eV in comparison with the He I PES values<sup>30</sup> of 12.74, 12.94, 13.48, 14.29, and 14.76 eV, respectively. The shake-up state described by  $1a_2^{-2}3b_1$  was also obtained at 14.70 eV with the intensity of 0.19; this state should correspond to the satellite observed at 13.8 eV by EMS with the intensity of 0.20.<sup>32</sup> Though the agreement of the IP was not

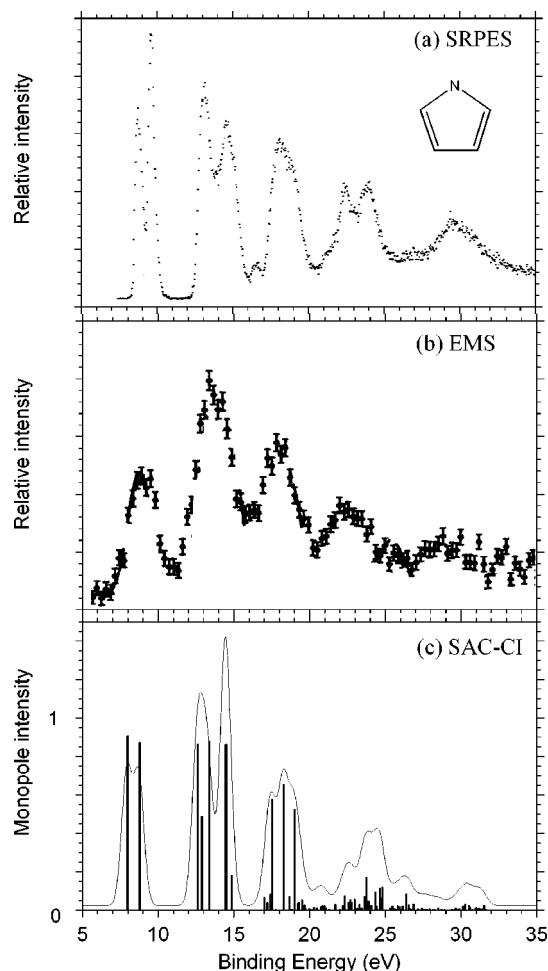


FIG. 4. Valence ionization spectra of pyrrole by (a) SRPES (Ref. 29), (b) EMS (Ref. 32), and (c) SAC-CI general-R method.

satisfactory for this satellite, the present calculation supported the picture of the splitting of the  $1b_1$  states. The peak at about  $\sim 12.5$  eV was attributed to the  $1b_1$  state by EMS (Ref. 32) and SRPES,<sup>29</sup> while it was assigned to the  $9a_1$  state by PIES.<sup>30</sup> The present calculation gave the ordering in the energy region of 12.5–15.0 eV as

$$9a_1, 1b_1 < 6b_2 < 1b_1 < 5b_2 < 8a_1,$$

though the energy separation between  $9a_1$  and  $1b_1$  is again very close like in furan. The ADC(3) calculation<sup>29</sup> gave the different ordering of the  $9a_1$  and  $1b_1$  states; this difference can be ascribed to the calculated energy of the  $9a_1$  state. By He I PES,<sup>30</sup> the satellite was observed at  $\sim 16.62$  eV. Correspondingly, the shake-up states were calculated at 17.01 and 17.42 eV, which were dominantly characterized as  $2b_1(\pi_2)^{-2}3b_1(\pi^*)$  and  $2b_1(\pi_2)^{-1}2a_2(\pi^*)1a_2(\pi_3)^{-1}$  states, respectively.

Next peaks corresponding to the ionization from the  $7a_1$ ,  $4b_2$ , and  $6a_1$  orbitals were observed as one band in SRPES (Ref. 29) and many satellite peaks were calculated with considerably distributed intensities by the ADC(3) method. In this work, the intensities were also distributed to many two-electron processes, however, the main lines of these states had relatively large intensities. These main lines were calculated to be at 17.51, 18.30, and 19.02 eV, which were very

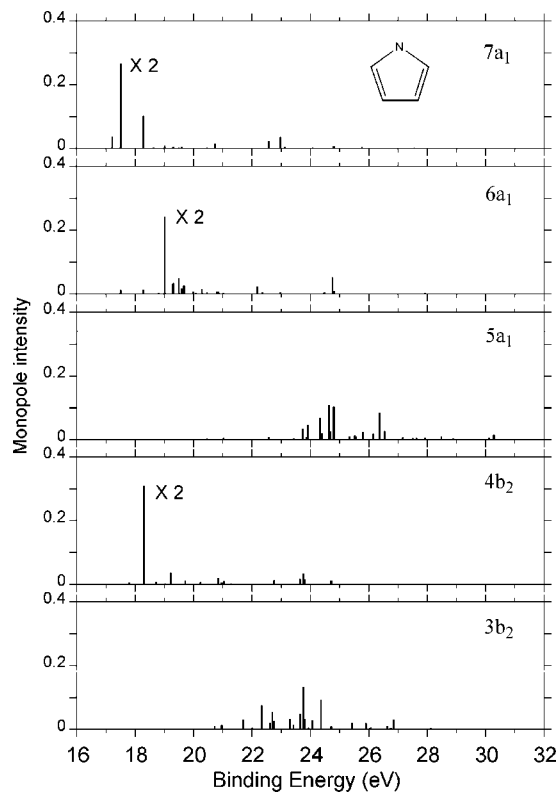


FIG. 5. MO contributions to monopole intensities in the energy region of 16–32 eV for pyrrole.

close in energy, and in good agreement with the He II PES (Ref. 23) values of 17.5, 18.1, and 18.8 eV. The two-electron processes of  $a_1$  symmetry are described by  $1a_2^{-2}na_1$  and  $2b_1^{-2}na_1$ .

In the inner-valence region, the peak split of the ionization from the  $5a_1$  and  $3b_2$  orbitals is remarkable like in furan. The present calculation reproduces the peak positions and the shape of the peaks in good agreement with SRPES (Ref. 29) and EMS.<sup>32</sup> The detailed experimental analysis of this energy region has not been reported, however, two split clusters of the peaks were observed in SRPES,<sup>29</sup> as cited in Fig. 4. In the present calculation, the peaks in the lower-energy side were attributed to the  $3b_2$  component and those in the higher energy were attributed to the components of both  $3b_2$  and  $5a_1$ , as shown in Fig. 5. This energy region is an interesting target for the detailed experimental study. In the energy region of  $\sim 30$  eV, the cluster of peaks whose intensities are due to the  $4a_1$  orbital exists; these peaks are lower in energy than those of furan reflecting the IP of  $2s$  orbital of the N atom.

## V. IONIZATION SPECTRUM OF THIOPHENE

Finally, the valence ionization spectrum of thiophene up to about 30 eV is discussed. The SRPES,<sup>28,29</sup> He I PES + PIES,<sup>30</sup> and He II PES (Ref. 24) works were reported for this molecule. The calculated spectrum was shown in Fig. 6 with the SRPES spectrum.<sup>29</sup> The detailed SAC-CI results for the outer- and inner-valence region were summarized with the experimental IPs in Table III.

TABLE II. Ionization potentials (IPs) (in eV), monopole intensities (in parenthesis), and main configurations of the outer- and inner-valence ionized states of pyrrole. Ionized states whose intensity is larger than 0.025 are shown.

State	Expt.			SAC-CI general-R	
	He I PES <sup>a</sup>	He II PES <sup>b</sup>	EMS <sup>c</sup>	IP (Intensity)	Main configuration ( $ C  \geq 0.4$ ) <sup>d</sup>
$1a_2$	8.28	8.21		7.98(0.91)	$0.93(1a_2^{-1})$
$2b_1$	9.26	9.20		8.78(0.87)	$0.91(2b_1^{-1})$
$9a_1$	12.74	12.60	13.0(1.0)	12.61(0.86)	$0.90(9a_1^{-1})$
$1b_1$	12.94		12.6(0.80)	12.77(0.49)	$0.69(1b_1^{-1}) + 0.53(1a_2^{-2}3b_1)$
$S$	(16.62)	13.7	13.8(0.20)	14.70(0.19)	$0.41(1b_1^{-1}) - 0.68(1a_2^{-2}3b_1)$
				17.01(0.07)	$0.56(2b_1^{-2}3b_1)$
				17.42(0.09)	$0.77(2b_1^{-1}2a_21a_2^{-1}) + 0.77(1a_2^{-1}2a_22b_1^{-1})$
				18.68(0.07)	$0.61(2b_1^{-2}3b_1)$
$6b_2$	13.48	13.0	13.7(1.0)	13.35(0.88)	$0.90(6b_2^{-1})$
$5b_2$	14.29	14.3	14.3(1.0)	14.49(0.86)	$0.90(5b_2^{-1})$
$8a_1$	14.76	14.8		14.57(0.86)	$0.90(8a_1^{-1})$
$7a_1$	17.44	17.5		17.20(0.04)	$0.84(1a_2^{-2}10a_1)$
				17.51(0.58)	$0.73(7a_1^{-1})$
				18.28(0.12)	$0.32(7a_1^{-1}) + 0.57(1a_2^{-2}13a_1) + 0.52(1a_2^{-2}11a_1)$
				22.57(0.04)	$0.69(1a_2^{-1}3b_15b_2^{-1})$
$4b_2$	18.00	18.1		22.98(0.06)	$0.52(2b_1^{-1}3b_19a_1^{-1}) + 0.40(1a_2^{-1}2a_29a_1^{-1})$
				18.30(0.65)	$0.78(4b_2^{-1})$
				19.23(0.04)	$0.76(1a_2^{-1}13a_12b_1^{-1}) + 0.53(1a_2^{-1}11a_12b_1^{-1})$
				20.85(0.03)	$0.54(2b_1^{-1}3b_16b_2^{-1}) - 0.54(1a_2^{-1}2a_26b_2^{-1})$
$6a_1$		18.8		19.02(0.53)	$0.70(6a_1^{-1})$
				19.30(0.04)	$0.63(9a_1^{-1}2a_21a_2^{-1})$
				19.32(0.04)	$0.68(2b_1^{-2}10a_1)$
				19.50(0.06)	$0.40(2b_1^{-1}8b_21a_2^{-1})$
				19.68(0.03)	$0.66(1a_2^{-2}12a_1)$
				22.18(0.03)	$0.47(2b_1^{-1}2a_26b_2^{-1})$
				24.76(0.07)	$0.48(1a_2^{-1}2a_28a_1^{-1}) + 0.45(2b_1^{-1}3b_18a_1^{-1})$
				21.70(0.03)	$0.51(2b_1^{-1}3b_15b_2^{-1})$
				22.33(0.08)	$0.49(1a_2^{-2}10b_2)$
				22.70(0.06)	$0.49(1a_2^{-1}3b_18a_1^{-1})$
				22.76(0.04)	$0.60(1a_2^{-1}3b_18a_1^{-1})$
				23.30(0.03)	$0.52(1a_2^{-1}16a_12b_1^{-1})$
$3b_2$				23.64(0.07)	$0.54(8a_1^{-1}2a_22b_1^{-1})$
				23.76(0.17)	$0.37(3b_2^{-1}) - 0.49(2b_1^{-1}3b_16b_2^{-1})$
				23.81(0.05)	$0.61(8a_1^{-1}2a_22b_1^{-1})$
				24.07(0.03)	$0.47(7a_1^{-1}3b_11a_2^{-1})$
				24.36(0.09)	$0.51(2b_1^{-1}16a_11a_2^{-1}) - 0.41(6a_1^{-1}3b_11a_2^{-1})$
				24.71(0.04)	$0.72(1a_2^{-1}2a_25b_2^{-1})$
				26.86(0.03)	$0.43(7a_1^{-1}2a_22b_1^{-1})$
				23.74(0.04)	$0.61(1a_2^{-1}10b_22b_1^{-1}) + 0.43(1a_2^{-2}16a_1)$
				23.92(0.05)	$0.58(4b_2^{-1}3b_11a_2^{-1})$
				24.33(0.07)	$0.51(7a_1^{-1}3b_12b_1^{-1})$
				24.64(0.11)	$0.33(5a_1^{-1}) - 0.43(7a_1^{-1}3b_12b_1^{-1})$
				24.68(0.03)	$0.32(2b_1^{-1}13a_11b_1^{-1})$
$5a_1$				24.81(0.12)	$0.32(5a_1^{-1}) - 0.45(2b_1^{-1}2a_25b_2^{-1})$
				25.80(0.03)	$0.73(6b_2^{-1}4b_11a_2^{-1})$
				26.37(0.09)	$0.57(1a_2^{-1}4b_16b_2^{-1})$
				26.54(0.03)	$0.33(2b_1^{-1}3b_18a_1^{-1})$
				30.28(0.03)	—
				30.52(0.03)	—
$4a_1$				31.52(0.03)	—

<sup>a</sup>Reference 30.<sup>b</sup>Reference 23.<sup>c</sup>Reference 32.<sup>d</sup>Main configurations with the coefficients of  $|C| \geq 0.4$  are shown; “—” means there are no main configurations.



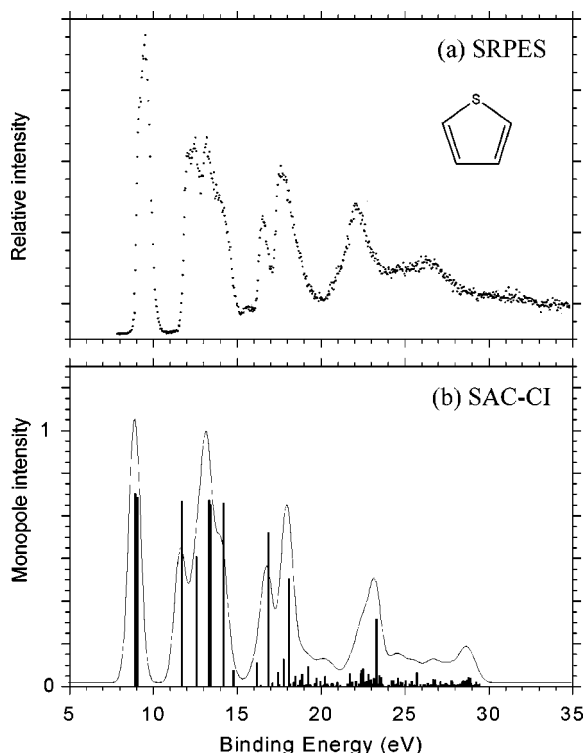


FIG. 6. Valence ionization spectra of thiophene by (a) SRPES (Ref. 29) and (b) SAC-CI general-*R* method.

It is generally agreed that the assignment of the outer-valence region of thiophene is in the ordering of

$$1a_2(\pi_3) < 3b_1(\pi_2) < 11a_1 < 2b_1(\pi_1) < 7b_2 \\ < 10a_1 < 6b_2 < 9a_1 < 5b_2 < 8a_1,$$

where the order of  $2b_1(\pi_1)$  and  $7b_2$  is reversed from that of the Koopmans picture. The present general-*R* calculation also gave the same ordering of the valence shell. The important feature of this spectrum is a satellite peak observed in the low-energy region at 15.66 eV by He I PES+PIES.<sup>30</sup>

For the five outer-valence ionized states from  $11a_1$  to  $6b_2$ , IPs were calculated to be 11.70, 12.56, 13.32, 13.41, and 14.16 eV in agreement with the experimental values<sup>30</sup> of 12.04, 12.49, 13.15, 13.71, and 14.26 eV, respectively. Among these states, the  $2b_1(\pi_1)$  state has the considerable interaction with the two-electron processes and has relatively small intensity as 0.61; the effect of higher *R* operators was important for this state. As the satellites of this peak, the shake-up states were calculated with the considerable intensity at 14.78, 16.19, and 17.42 eV; these states were characterized as  $1a_2^{-2}4b_1$ ,  $3b_1^{-2}4b_1$ , and  $3b_1^{-1}2a_21a_2^{-1}$  as those in furan and pyrrole. Similar splitting was also obtained in the ADC(3) calculation.<sup>29</sup> The satellite calculated at 16.19 eV was attributed to the observed peak at 15.66 eV.<sup>30</sup>

Among the peaks originating the  $9a_1$ ,  $5b_2$ , and  $8a_1$  orbitals, the ionization from the  $9a_1$  orbital was calculated to be lower by about 1 eV than the other two states as shown in Fig. 6 and this state was observed as a separated peak in SRPES.<sup>29</sup> The  $5b_2$  and  $8a_1$  states were dominantly single peak at almost the same energy and there were few satellites with small intensities in the higher-energy region, which

shows that the electron correlations of these states are not so significant in comparison with those of furan. More detailed intensity contributions in the energy region of 16–32 eV were shown in Fig. 7.

The characteristic spectrum shape in the inner-valence region was well reproduced in the present calculation. One prominent peak was observed at 22.1 or 22.3 eV by SRPES (Ref. 28) and He II PES,<sup>24</sup> respectively. In the present result, this peak was attributed to the ionization from the  $4b_2$  orbital and the  $4b_2$  intensity was not distributed to the shake-up states around it, which is different from the satellite peaks in this region of furan and pyrrole. On the other hand, the  $7a_1$  state interacts with many two-electron processes and there is no strong peak with large intensity. This characteristic feature is different from those obtained in the previous theoretical works.<sup>27,29</sup> The peak observed at 20.8 or 22.1 eV by SRPES (Ref. 29) and He II PES,<sup>24</sup> respectively, was assigned to many satellite peaks of the  $7a_1$  component and also to some contributions from the  $4b_2$  component.

In the higher-energy region of strong peak assigned to the  $4b_2$  peak, the continuous satellite peaks were observed. Accordingly, the present calculations gave many satellites in this energy region and the dominant components of the intensity were due to the  $7a_1$ ,  $4b_2$ ,  $7a_1$ ,  $7a_1+6a_1$ , and  $6a_1$  orbitals for the peaks observed at 23.2, 24.4, 25.7, 26.8, and 28.3 eV by SRPES,<sup>28</sup> respectively. Note that the  $6a_1$  peaks start from the low-energy region in comparison with the corresponding states of furan and pyrrole.

## VI. CONCLUSION

We have applied the SAC-CI general-*R* method to the valence ionization spectra of furan, pyrrole, and thiophene in both the outer- and inner-valence regions. The present calculations well reproduced the experimental spectra observed by SRPES,<sup>28,29</sup> EMS,<sup>31,32</sup> and He I PES (Refs. 19 and 30) with respect to the peak positions and the intensities.

For the outer-valence region, it was shown that the  $\pi_1$  state strongly interacts with the shake-up states,  $\pi_3^{-2}\pi^*$ ,  $\pi_2^{-2}\pi^*$ , and  $\pi_2^{-1}\pi_3^{-1}\pi^*$ , distributing the considerable intensity; the effect of higher *R* operators was important for these states. These interactions with the shake-up states result in the split peaks and the outer-valence satellites, both of which are in agreement with the experiments. The previous theoretical calculation<sup>29</sup> also gave the similar splittings of the  $\pi_1$  states in all three molecules, which confirms the present results. The relative intensities of these states calculated by the present method also agree with those measured by EMS. The present calculation gave the consistent interpretation with the experimental observation for the outer-valence ionized states.

For the inner-valence region, the detailed analysis of the intensity distributions was performed. For furan, theoretical intensity distributions were successfully compared with the experimental values by EMS. Theoretical intensity distributions were also calculated for pyrrole and thiophene. The interactions of both the  $3b_2$  and  $5a_1$  states with the shake-up

TABLE III. Ionization potentials (IPs) (in eV), monopole intensities (in parenthesis), and main configurations of the outer- and inner-valence ionized states of thiophene. Ionized states whose intensity is larger than 0.025 are shown.

State <sup>a</sup>	Expt.			SAC-CI general-R	
	He I PES <sup>b</sup>	He II PES <sup>c</sup>	SRPES <sup>d</sup>	IP (Intensity)	Main configuration ( $ C  \geq 0.4$ ) <sup>e</sup>
$1a_2$	8.96	8.87	9.0	8.92(0.90)	$0.93(1a_2^{-1})$
$3b_1$	9.58	9.52	9.5	9.05(0.89)	$0.91(3b_1^{-1})$
$11a_1$	12.04	12.1	12.0	11.70(0.87)	$0.90(11a_1^{-1})$
$2b_1$	12.49	12.7	12.5	12.56(0.61)	$0.76(2b_1^{-1}) + 0.38(1a_2^{-2}4b_1)$
				14.78(0.08)	$0.79(1a_2^{-2}4b_1)$
$S$	15.66			16.19(0.11)	$0.33(2b_1^{-1}) + 0.75(3b_1^{-2}4b_1)$
				17.42(0.07)	$0.85(3b_1^{-1}2a_21a_2^{-1}) + 0.75(1a_2^{-1}2a_23b_1^{-1})$
$7b_2$	13.15	13.3	13.2	13.32(0.87)	$0.90(7b_2^{-1})$
$10a_1$	13.71	$\sim 13.9$	13.9	13.41(0.85)	$0.89(10a_1^{-1})$
$6b_2$	14.26	14.3	14.4	14.16(0.86)	$0.89(6b_2^{-1})$
$9a_1$	16.52	16.6	16.6	16.84(0.72)	$0.82(9a_1^{-1})$
$5b_2$	17.62	17.6	17.6	18.05(0.50)	$0.69(5b_2^{-1}) - 0.34(1a_2^{-1}4b_111a_1^{-1})$
				18.09(0.04)	$0.66(1a_2^{-1}4a_13b_1^{-1}) + 0.52(1a_2^{-1}15a_13b_1^{-1})$
				18.45(0.05)	$0.68(3b_1^{-1}14a_11a_2^{-1})$
				18.76(0.03)	$0.63(1a_2^{-1}4b_111a_1^{-1}) - 0.59(7b_2^{-1}4b_13b_1^{-1})$
				18.85(0.06)	$0.73(7b_2^{-1}4b_13b_1^{-1}) + 0.47(1a_2^{-1}4b_111a_1^{-1})$
				20.25(0.05)	$0.63(3b_1^{-1}4b_17b_2^{-1})$
$8a_1$				17.78(0.13)	$0.33(8a_1^{-1}) + 0.67(7b_2^{-1}4b_11a_2^{-1})$
					$-0.62(11a_1^{-1}4b_13b_1^{-1})$
	18.30	$\sim 18.3$	18.4	18.07(0.47)	$0.66(8a_1^{-1})$
				19.24(0.09)	$0.55(3b_1^{-1}4b_111a_1^{-1})$
				19.72(0.04)	$0.49(11a_1^{-1}2a_21a_2^{-1}) + 0.41(3b_1^{-2}14a_1)$
				21.73(0.06)	$0.68(11a_1^{-1}4b_16b_2^{-1})$
$7a_1$		$\sim 22.1$	20.8	22.39(0.07)	$0.54(11a_1^{-1}4b_12b_1^{-1})$
				22.50(0.08)	$0.37(3b_1^{-1}11b_21a_2^{-1})$
				22.72(0.03)	$0.51(1a_2^{-2}16a_1)$
				22.82(0.06)	$0.43(3b_1^{-1}12b_21a_2^{-1})$
				22.99(0.03)	$0.37(3b_1^{-1}2a_27b_2^{-1})$
				23.17(0.04)	—
				23.23(0.03)	$0.45(3b_1^{-2}20a_1)$
$a$			23.2	23.28(0.07)	—
				23.47(0.05)	$0.42(3b_1^{-1}2a_26b_2^{-1})$
				23.57(0.04)	$0.40(1a_2^{-1}11b_23b_1^{-1})$
				24.60(0.04)	$0.40(7b_2^{-1}8b_211a_1)$
				25.06(0.03)	$0.40(9a_1^{-1}2a_21a_2^{-1})$
				25.41(0.03)	$0.40(11a_1^{-1}8b_27b_2^{-1})$
$c$			25.7	25.71(0.07)	$0.41(11a_1^{-1}8b_27b_2^{-1}) + 0.41(5b_2^{-1}4b_11a_2^{-1})$
$d$			26.8	26.68(0.04)	—
$4b_2$				22.09(0.03)	$0.52(3b_1^{-1}2a_211a_1^{-1}) - 0.49(3b_1^{-1}2a_210a_1^{-1})$
				22.38(0.06)	$0.49(3b_1^{-1}2a_211a_1^{-1})$
		$\sim 22.3$	22.1	23.29(0.32)	$0.55(4b_2^{-1})$
				24.19(0.03)	$0.43(5b_2^{-1}4b_13b_1^{-1}) - 0.42(8a_14b_11a_2^{-1})$
$b$			24.4	24.30(0.03)	$0.48(2b_1^{-1}13a_11a_2^{-1})$
$6a_1$			26.8	26.80(0.03)	$0.34(3b_1^{-1}4b_18a_1^{-1})$
				27.77(0.03)	—
$e$			28.3	28.48(0.03)	$0.36(7b_2^{-1}9b_211a_1^{-1})$
				28.68(0.03)	$0.33(2b_1^{-1}17a_13b_1^{-1})$
				28.79(0.04)	$0.44(5b_2^{-1}2a_23b_1^{-1})$
				28.89(0.04)	—

<sup>a</sup>The peak numbers, a–e, in the inner-valence region are due to Ref. 28.

<sup>b</sup>Reference 30.

<sup>c</sup>Reference 24.

<sup>d</sup>Reference 28.

<sup>e</sup>Main configurations with the coefficients of  $|C| \geq 0.4$  are shown; “—” means there are no main configurations.

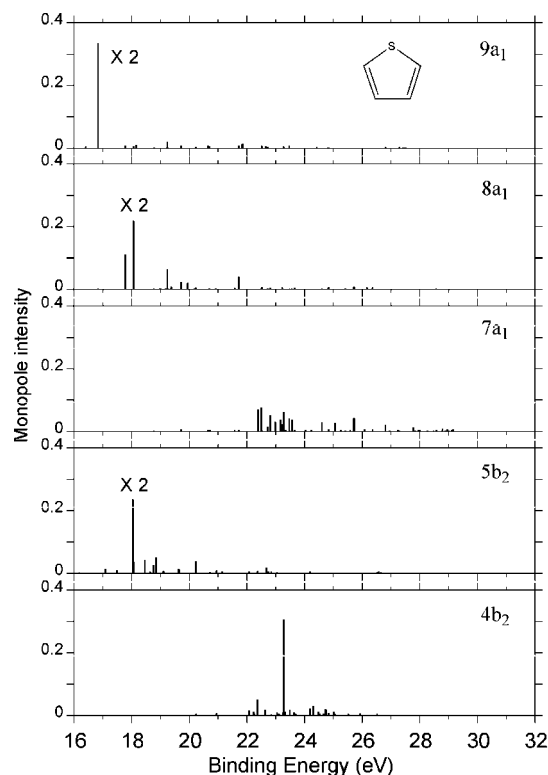


FIG. 7. MO contributions to monopole intensities in the energy region of 16–32 eV for thiophene.

states were remarkable for furan and pyrrole, while the  $4b_2$  of thiophene did not strongly interact with the shake-up states and had relatively large intensity.

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